

# REACTIONS OF NITRIC OXIDE WITH CARBONS : THE KINETICS OF NO CHEMISORPTION ON CARBON

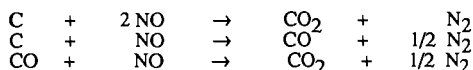
Hsisheng Teng, E. M. Suuberg and J. M. Calo

Division of Engineering  
Brown University  
Providence, Rhode Island 02912

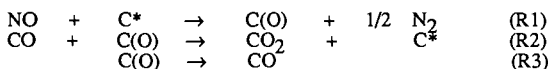
**Keywords:** Nitric Oxide, Carbon, Chemisorption

## INTRODUCTION

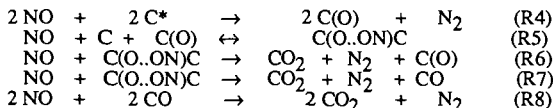
The fact that NO formed during a combustion process can be heterogeneously reduced by carbonaceous solids is well known<sup>1</sup>. There have been a modest number of studies of various aspects of NO-char studies in the last 30 years(e.g. ref. 2-6). In general, the overall reaction has been reported to actually include the following stoichiometric reactions :



It has been noted that the reaction of NO with char parallels in some respects the reaction of O<sub>2</sub> with chars, in that surface oxide intermediates play a role in the mechanism. For example, it has been reported<sup>2</sup> that at temperatures between 123 and 473 K, there are carbon-oxygen complexes formed on the char surface, with the release of N<sub>2</sub> as a gaseous product. The NO-char reaction studies reported by previous workers focus mainly on the investigation of the global kinetics during the pseudo steady state gasification. From the global kinetic results, one group<sup>4</sup> proposed a mechanism for the reaction of carbon with NO as follows :



This reaction scheme was used to derive a Langmuir-Hinshelwood type rate expression for the rate of NO consumption. The authors of this model noted its shortcoming in terms of failing to correctly predict an overall first order rate with respect to NO pressure. An alternative mechanism<sup>2</sup> is somewhat more elaborate :



The original presentation of this model included two reversible steps of form (R5), representing the formation of the two different types of C(O..ON)C complexes that react according to (R6) and (R7). There is general agreement that the first step is chemisorption of NO at almost any temperature of relevance. It probably involves addition of NO in an N-down configuration<sup>7</sup>, followed by release of N<sub>2</sub> and formation of carbon oxide surface complexes, as suggested in (R4). In our recent study<sup>6</sup>, we found that N<sub>2</sub> is a significant product during desorption from NO oxidized char even at high temperatures(> 1000 K). Although (R5) of the above mechanism represents the existence of long-lived N containing complexes on the surface, the C(O..ON)C complex with the weak physical bonding suggested by the authors<sup>2</sup> still most likely cannot represent the long-lived N containing complexes we have observed. It might then be possible that the C(O..ON)C complex is actually a chemisorbed complex, and that the desorption of N<sub>2</sub> we have observed involves the reverse of reaction (R5) followed by (R6), (R7) or (R8). We however see no evidence of desorption of NO as

such, except at low temperatures (see below). Thus we feel it most likely that the reaction (R4) does not proceed as indicated in a single step, and that there is some way of forming N containing surface species that can desorb as  $N_2$  even in the absence of NO. Furthermore, the above model is deficient in not including a straight desorption route for formation of  $CO^0$ .

The validity of (R1) or (R4) as the route for NO sorption is thus in doubt. A more sophisticated sorption model should be constructed to explain the observations. This paper presents some results of NO-char sorption at low temperatures ( $< 523$  K), at which the gasification of char is negligible.

## EXPERIMENTAL

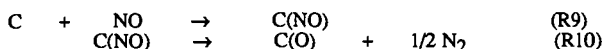
A standard thermogravimetric device (TGA) was used for the present study. Experiments were performed in a static system, in He/NO mixtures at 101 kPa total pressure. The volume of the vessel was large enough to ensure that under any reaction conditions, the consumption of NO was not significant. Pulverized char samples (50–100 mg) were held in a quartz bucket suspended in the heated zone of a quartz tube. A thermocouple placed within a few millimeters of the bucket served to indicate the temperature of the sample. The vessel could be purged following an experiment, and the contents analyzed by gas chromatography.

The chars used in present study were derived from phenol-formaldehyde resins. These resin have structure features similar to those in coals, but contain few catalytic impurities. These can be controlled to very low levels in synthesis. The resin char was prepared by pyrolysis of the phenol-formaldehyde resin in a nitrogen environment at 1323 K for 2 hours, then ground and sieved to give the desired particle size. The surface of the char was cleaned of oxides prior to NO sorption experiments by heating the sample to 1223 K in high purity helium for at least 2 hours.

NO sorption experiments were performed after surface cleaning by lowering the temperature of the sample from 1223 K to the desired sorption temperature, and then quickly introducing the desired NO/He mixture. Three sequences (I, II and III) were used to monitor the NO uptake. Sequence I started with a continuous monitoring of NO uptake for at least 24 hours until the mass gain is undetectable (i.e.  $\pm 10$   $\mu$ g). Sequence II involved performing sorption, as in sequence I, to a constant mass uptake, followed by a series of changes in temperature, which affected the mass on the surface. Each temperature step lasted for 10 hours until there was no longer any detectable variation of the sample mass. Sequence III also involved performing sequence I, followed by an abrupt replacement of NO atmosphere by pure helium. After a period of monitoring the sample mass in helium, until there was no detectable mass variation, the original mixture of NO/He was reintroduced to the system, and the mass was monitored. Sequence III was performed under isothermal conditions.

## RESULTS AND DISCUSSION

The NO uptake curves and the final mass uptake in sequence I sorption at different experimental conditions are shown in Fig. 1 and Table I, respectively. The shape of the NO uptake curve is similar to that of  $O_2$  chemisorption<sup>8</sup> on char. However it was found that the amount of NO uptake decreases with the increase of the temperature of char sample, while there was always an increase of the amount of  $O_2$  uptake with increase in temperature<sup>8</sup>. These results suggested that gasification of the char by NO might be occurring in this temperature range, and that the increase in the rate of sorption with increasing temperature might have been counterbalanced by an increase in the rate of a gasification step. However, no mass decline was observed after four days of sorption in an NO atmosphere, unlike the case in  $O_2$  chemisorption when the rate of gasification ultimately overtakes the rate of chemisorption, as all the surface sites are filled. Furthermore, only small amount of  $CO_2$  were formed (no CO was found) after the long period of chemisorption. These amount of  $CO_2$  were negligible in comparison to the large decreases in mass seen with increasing temperature. Finally, according to our previous studies, the steady state gasification of char by NO proceeds at an undetectable level at temperatures lower than 673K. Therefore, we rule out gasification of char by NO in this temperature range. Combining the above results with the claim that there exist long-lived N containing complexes on the NO oxidized char surface, as shown in our recent studies<sup>9</sup>, one can conclude that NO sorption on char with the simultaneous release of  $N_2$ , as described by (R1), is not the route for NO sorption on char. A better model to describe this chemisorption might be as follows



In this model, both C(O) and C(NO) exist on the char surface. The C(NO) complex above can represent the N containing complex on NO oxidized char, and N<sub>2</sub> can be released through (R10) during desorption. The release of N<sub>2</sub> in (R10) would be activated by raising the temperature of the char sample, therefore the mass uptake during NO chemisorption on char would be less at higher temperature owing to the the N<sub>2</sub> release. The possibility of the backward reaction of (R9) to release NO should be also considered, and will be discussed later in this paper.

The results of sequence II sorption are given in Table 2. It shows that the mass of the sample decreased when the temperature was raised, and mass was regained on the sample when the temperature was lowered to the original value. The sequence is shown in Table 2. Mass is always lost with an increase in sample temperature. Returning to the same temperature results in a significant regain of mass (e.g. compare 5 and 6), but does not always restore the mass on the surface to the original values - compare steps 1 and 6, 4 and 8, 3 and 9, 2 and 10. The process appears to reach a measure of reversibility with continued cycling, however (compare 6 and 11). Experimental work on this this point continues. Thus the mass loss or gain of the sample was found to be somewhat reversible with respect to the temperature of the sample. It appears from these experiments that there may be a reversible pathway for NO chemisorption. This will be further supported below. Since there are some complexes that cannot be removed by these procedures, there must be an essentially irreversible pathway for sorption as well (recall that there are N-complexes stable up to > 1000 K). As mentioned above in discussing sequence I, no significant amounts of carbon oxides were found during sorption in this temperature range. Therefore, reaction (R10) is the candidate for the irreversible loss of mass during heating in this temperature range.

The results of sequence III are shown in Fig. 2 and Table 3. The mass variation was reversible with respect to the partial pressure of NO, and, therefore, contributed to by NO uptake or release. The results in Fig. 2 can be well described by the low pressure limit of Langmuir sorption isotherm and a temperature dependent equilibrium constant:

$$w = k_0 \cdot \exp[-Q/RT] \cdot P_{\text{NO}}$$

where  $k_0$  is the preexponential factor in g/(m<sup>2</sup>·kPa),  $w$  is the NO uptake in g/m<sup>2</sup>,  $P_{\text{NO}}$  is NO partial pressure in kPa, and  $Q$  is the heat of reversible sorption in kJ/mole. From a plot of  $\ln(w)$  vs.  $1/T$ , the value  $7.63 \cdot 10^{-13}$  g/(m<sup>2</sup>·kPa) for  $k_0$  and -41.7 kJ/mol (i.e. exothermic) for  $Q$  were determined. The temperature dependence of the data of Table 3 is, incidentally, entirely consistent with that of the data of Table 2 considering only the reversible part of the chemisorption. The conclusion is that the reversible sorbate in sequence II is NO. Therefore, there must exist a reversible chemisorption pathway in addition to the irreversible (R9):



with a value of 41.7 kJ/mol as the heat of exothermic sorption, as described above. The heat of sorption of this value is much higher than that of usual physisorption which is usually less than 20 kJ/mol. This might be attributable to the free radical nature of NO molecules and thus an ability to form bonds stronger than physical bonds.

Similar to the O<sub>2</sub> chemisorption<sup>9</sup>, the chemisorption behavior of NO can also be well described by the Elovich equation:

$$dq/dt = b \cdot \exp[-a \cdot q]$$

where  $a$  and  $b$  are fitting parameters, and  $q$  is the amount of mass uptake normalized by the total amount of mass uptake at the end of the run. The results given in Table 4 were determined by subtracting the contribution of the reversible step (R11), assuming it to occur instantaneously at time zero. It is unclear whether this is strictly speaking justified, but the rate of the reversible step appears to be quite high, compared to the overall rate for sorption, so the approximation may not be bad. Table 4 clearly shows that the  $b$  value, the extrapolated sorption rate at zero coverage, is roughly

proportional to NO pressure in the case of 423 K sorption temperature. This suggests that the rate of irreversible NO chemisorption (R9) is proportional to NO pressure. The value of  $a$  is not a function of NO pressure in the case of 423 K sorption, suggesting that the variation of kinetics of irreversible sorption with coverage is unaffected by the changing of NO pressure. It is of interest to note that the  $b$  value decreases with the sorption temperatures, which would imply a negative activation energy for the initial chemisorption. There is no physical significance to this result, because the role of  $N_2$  release through (R10) has been neglected in the calculation. This aspect of the process will receive further attention.

The apparent activation energies of chemisorption (including both irreversible and reversible routes) at different extents of surface coverage, determined from the rates of mass uptake at several sorption temperatures, are shown in Fig. 3. The increase of the apparent activation energy, as shown in Fig. 3, from negative to positive values in the course of site filling suggests that the rate of  $N_2$  release slows down compared to that of NO uptake when there are more complexes accumulated on the char surface. The reasons for this are not yet fully understood, and experiments are under way to verify the role of the  $N_2$  release processes.

## CONCLUSIONS

The chemisorption of NO on char surface is not always immediately followed by the release of  $N_2$  from the dissociation of the NO molecule. The complexes C(NO) as well as C(O), derived from NO chemisorption, can both exist on char surface. The rate of NO chemisorption on clean char surface is roughly proportional to NO pressure. There are both irreversible and reversible routes for chemisorption of NO on carbon.

## ACKNOWLEDGEMENT

We gratefully acknowledge the support of the USDOE through grant DEFG22-87PC79929 and the experimental assistant of Mr. William D. Lilly.

## REFERENCES

1. Pereira, F. J., Beer, J. M., Gibbs, B. and Hedley, A. B., 15th Symposium(International) on Combustion, The Combustion Institute, Pittsburgh, 1149(1974)
2. Smith, R. N., Swinehart, J. and Lesnini, D., Journal of Physical Chemistry, 63, 544(1959)
3. Furusawa, T., Kunil, D., Oguma, A. and Yamada, N., International Chemical Engineering, 20, No. 2, 239(1980)
4. Chan, L. K., Sarofim, A. F. and Beer, J. M., Combustion and Flame, 52, 37/45(1983)
5. Teng, H., Suuberg, E. M., Calo, J. M. and Hall, P. J., Proc. 19th Conf. on Carbon, 574 (1989)
6. Suuberg, E. M., Teng H. and Calo, J. M., 23rd Symposium(International) on Combustion, The Combustion Institute, in press(1990)
7. Zarifyanz, Y. A., Kiselev, V. F., Lezhnev, N. N., and Nikitina, O. V., Carbon, 5, 127(1967)
8. Suuberg, E. M., Calo, J. M. and Wojtowicz, M., ACS, Division of Fuel Chemistry, Preprint, 31(3), 186(1986)
9. Suuberg, E. M., Wojtowicz, M. and Calo, J. M., Carbon, 27(3), 431(1989)

Table 1. Total amount of mass uptake( $q_f$ ) for NO adsorption on char in sequence I

$P_{NO}$	10.1 kPa				4.04 kPa
Temperature(K)	523	473	423	423	423
$q_f (g/m^2) \cdot 10^5$	1.59	2.20	2.71	2.48	2.08

Table 2. Variation in mass of sorbed species (m) for the reaction sequence II at constant NO partial pressure of 10.1 kPa

Step	1	2	3	4	5	6	7	8	9	10	11
Temp.(K)	$m(g/m^2) \cdot 10^6$										
373	34.20					30.88					30.86
398		30.75								28.26	
423			28.73						27.30		
448				27.48				26.93			
473					26.90		26.90				

Table 3. Amount of reversible NO uptake(w) at different temperatures and NO pressures in sequence III

$P_{NO}(kPa)$	$w (g/m^2) \cdot 10^6$		
	10.1	4.04	2.02
Temperature(K)			
373	4.29	1.72	0.889
398	1.80	0.693	0.320
423	0.849	0.319	0.182
448	0.512		
473	0.297		

Table 4. The Elovich parameters for NO chemisorption on char

$P_{NO}$	10.1 kPa			4.04 kPa
Temperature(K)	523	473	423	423
* a	4.55	5.59	5.70	5.78
** b · 100	3.06	3.70	4.17	1.73

\* a is a non-dimensional quantity.

\*\* b is in units of  $\text{min}^{-1}$

